STUDIES ON THE EXPLOSIONS UNDER HIGH PRESSURES, III

The Explosions of Acetylene mixed with Oxygen or Air and the Effects of Pressure and of Added Substances

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Introduction

In the previous paper, Kiyama, Osugi and Teranishi reported on the explosions of acetylene mixed with oxygen under high pressure and the effects of added substances, i. e. carbon tetrachloride and water, to the explosion limits, and also reported briefly on the results of the preliminary experiments on the explosions of acetylene mixed with air[1]. In the present paper the author will mention on (1) the correctional results of the effect of water on the explosion limits of acetylene—oxygen mixtures, (2) the effect of methanol on the explosion limits of acetylene—O_2 mixtures, (3) the explosion limits of acetylene—air mixtures, and (4) the effect of pressure on the explosion limits of acetylene mixed with air or oxygen.

Experimentals

The experimental apparatus and the procedures are as described in the previous paper. The reaction gases are mixed and stored in the steel reservoir of about 55 cc in capacity, and then the gas mixtures are poured rapidly into the reaction vessel (4 cm and 1 cm in outer and inner diameters respectively and 9.42 cc in capacity) which is previously evacuated and heated to a given temperature. The occurrences of explosions at a given pressure in the reaction vessel are perceived by the sound and are observed by means of a membrane pressure gauge. The membrane pressure gauge[2] is constructed with a spring steel membrane (0.8~3.0 mm in thickness and 44 mm in effective diameter) and a mirror which rotates proportionally to the deflection of the membrane due to pressure change. The pressure changes are measured from the displacements on a scale of light spot reflected from the mirror and also recorded with time by means of a wire resistance strain meter and an electromagnetic oscillograph. The strain meter measures the changes of the electric resistance of the gauge which is cemented on the membrane of the pressure gauge. In the experiments of the effects of added substances, about 15 cc of water or methanol is stored in the reservoir of gas mixture and the vapor is mixed with the reaction gas.

1) R. Kiyama, J. Osugi and H. Teranishi, *This Journal*, 24, 41 (1954)
2) R. Kiyama, J. Osugi and H. Teranishi, *ibid.*, 24, 81 (1954)

Experimental Results and Considerations

The effect of water on the explosion limits of acetylene—oxygen mixtures

As described in the previous paper, the violence of the explosion of $C_2H_2—O_2$ mixture seems to become severer when water vapor is added. It was, therefore, favorable to make the connecting pipe line between the reaction vessel and the reservoir of gas mixture fine and long for the explosion to be prevented from propagating to the reservoir. However, a doubt was arisen on the mixing of reaction gases in the connecting pipe. Therefore the mixing has been re-examined and the correctional experiments have been performed to determine the effects of water.

The results of the experiments on the explosion limits of $C_2H_2—O_2$ mixtures under such conditions as the total pressure is $10 kg/cm^2$ and the partial pressure of the water is $0.02\sim0.03 kg/cm^2$ are shown in Fig. 1. Curve a shows the explosion limits of $C_2H_2—O_2$ mixtures without any added substance, curve b shows the limits in the presence of the water vapor reported in the previous paper, and the shaded part shows the results of the correctional experiments. Comparing the latter with curve c, that is the limits in the presence of CCl_4 vapor whose partial pressure is about $0.15 kg/cm^2$, it is shown that in the cases of adding H_2O, even though whose vapor pressure is one-seventh of that of CCl_4, the temperatures of explosion limits are almost equally elevated as in the cases of adding CCl_4.

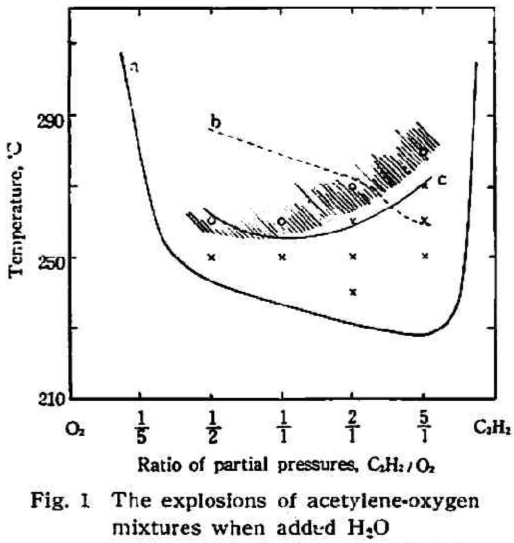

Fig. 1 The explosions of acetylene-oxygen mixtures when added H_2O
○: exploded ×: not exploded
(total pressure: $10 kg/cm^2$)

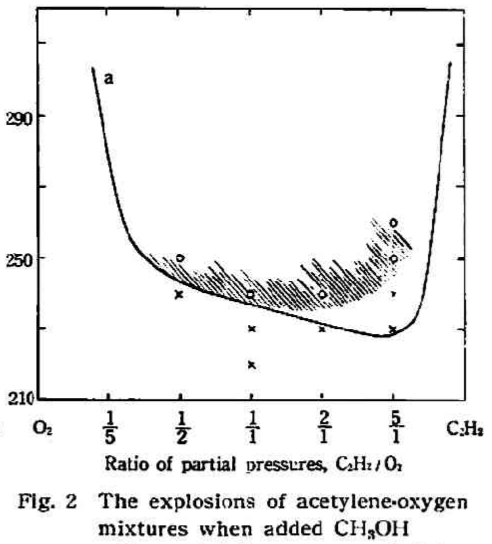

Fig. 2 The explosions of acetylene-oxygen mixtures when added CH_3OH
○: exploded ×: not exploded
(total pressure: $10 kg/cm^2$)

The effect of methanol on the explosion limits of acetylene—oxygen mixtures

In the same manner as in the cases of adding CCl_4 and H_2O, the measurements have been performed on the effect of adding CH_3OH to the explosion limits of $C_2H_2—O_2$ mixtures. Aldehydes having been removed, about 15 cc of CH_3OH are distilled and stored in the gas reservoir and its partial pressure is 0.17~0.2 kg/cm² in the reaction gas.

The results of the experiments under 10 kg/cm² of total pressure are shown by the shaded part in Fig. 2. Comparing with the limits of C_2H_2—O_2 mixtures without any added substance (curve a), no effect is observed except under such conditions as the partial pressure ratio is $C_2H_2/O_2>2/1$, where the added methanol elevates the limits by a degree slightly higher than 10°C, that is higher than the accuracy of determining the temperature of explosion limits. Methanol itself, on the contrary to CCl_4 and H_2O, is combusible in oxygen atmosphere but the oxidation process is not elucidated clearly. The thermal ignition temperature of methanol (461~555°C at 1 atm[3]) is higher than that of C_2H_2. Although the effect of methanol can not be discussed exactly but the experimental results show neither elevating nor descending effect on the temperature of explosion limits of C_2H_2—O_2 mixtures.

Explosion limits of acetylene—air mixtures In the previous paper, it was reported that the violence of the explosion of C_2H_2—air mixture was much weaker than that in the case of C_2H_2—O_2 mixture, and the occurrence of the explosion could scarcely be perceived neither by the sound nor by the displacement of the light spot on the scale, and yet could be determined from the pressure change curve which was recorded by means of the strain meter and electromagnetic oscillograph. A few results of the preliminary experiments were reported, but reliable explosion limits were not yet determined in the previous paper. Therefore a number of ex-

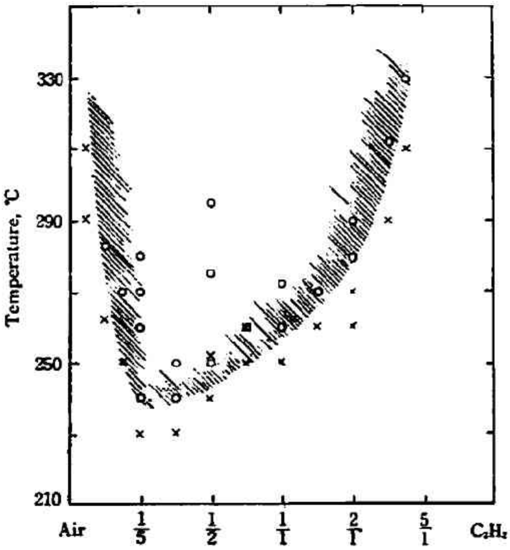

Fig. 3 The explosions of acetylene-air mixtures
○: exploded ×: not exploded
(total pressure: 10–12 kg/cm²)

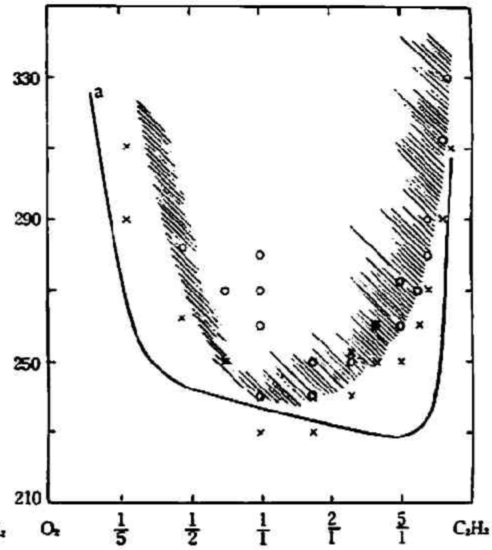

Fig. 4 A The explosions of acetylene-air mixtures
abscissa taken as the ratio of the partial pressures of C_2H_2 and O_2

3) B. P. Mullins, *Spontaneous Ignition of Liquid Fuels*, p. 67 (1955)

periments have been performed, taking care of the complete mixing of C_2H_2 and air, to determine the explosion limits.

The results of the experiments under the total pressure of 10~12 kg/cm^2 are shown in Fig. 3. The explosion limits can be determined clearly and become a smooth curve. The minimum temperature of the limits, 230~240°C under the condition of C_2H_2/air $=1/5 \sim 1/2$ is about 150°C lower than that reported by Rimarski and Konschak[4] for the explosion under 1 atm, and this difference, as will be described in the next section, is due to the effect of the total pressures of the reaction gases. Converting the results into the figure where the ratios of partial pressure of C_2H_2 to that of O_2 in air are taken as abscissa, the explosion limits of C_2H_2—air mixtures are shown by the shaded part in Fig. 4 A. The minimum temperature which is found under the condition that C_2H_2/O_2 is about 1, shows no difference from that of C_2H_2—O_2 mixture (curve a). The sums of the partial pressures of C_2H_2 and O_2 are about 4 kg/cm^2 in the C_2H_2—air mixture and 10 kg/cm^2 in the C_2H_2—O_2 mixture, but in the former mixture N_2 is contained and the total pressure is 10 kg/cm^2. Under the condition of the total pressure 10 kg/cm^2, the differences of the explosion temperatures between the both curves is not observed. Converting also the results into the figures where the percentages of the content of O_2 and C_2H_2 are taken as abscissa respectively, the explosion limits of C_2H_2—air mixtures are shown by the shaded parts in Fig. 4 B and Fig. 4 C respectively. In both

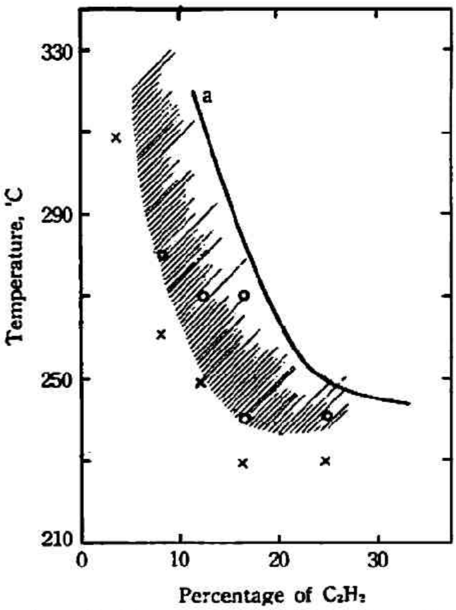

Fig. 4 C The explosions of acetylene-air mixtures
abscissa taken as the percentage of C_2H_2

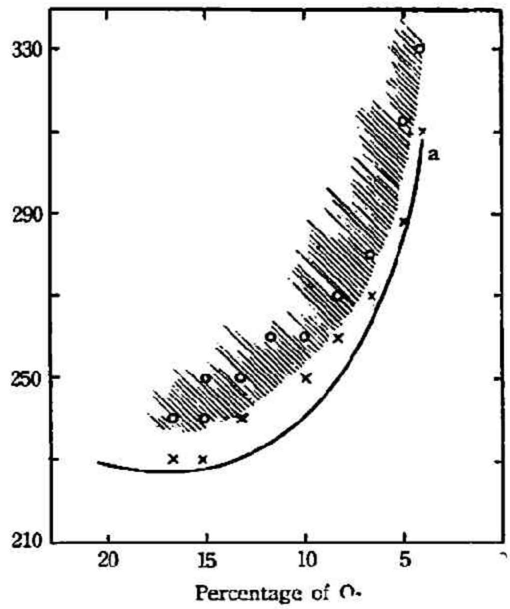

Fig. 4 B The explosions of acetylene-air mixtures
abscissa taken as the percentage of O_2

4) W. Rimarski and M. Konschak, *Azetylen in Wiss. und Ind.*, **31**, 24 (1928)

figures, curves a show the explosion limits of $C_2H_2-O_2$ mixtures. In Fig. 4 B, both curves show the minimum temperatures at the composition of about 16% O_2, where C_2H_2/O_2 is 1 and the sum of the partial pressures of C_2H_2 and O_2 is 4kg/cm^2 for the C_2H_2—air mixture, and C_2H_2/O_2 is 5/1 and total pressure is 10kg/cm^2 for $C_2H_2-O_2$ mixture. The former mixture contains a large amount of N_2 and the latter contains excess amount of C_2H_2. Comparing both limits, in the O_2 poor range, it is shown that the explosion limits are elevated when the excess of C_2H_2 is replaced by N_2 under the condition of constant contents of O_2 and the constant total pressure. On the other hand, in the C_2H_2 poor ranges, the explosion limits for C_2H_2—air mixtures are, as shown in Fig. 4 C, lower than that for $C_2H_2-O_2$ mixture under the same content of C_2H_2. From this fact the explosion limits are descended when the excess amount of O_2 is replaced by N_2.

Effect of pressure on the explosion temperature of acetylene mixed with air or oxygen The relations between total pressures and explosion temperatures have been measured, and the results on the gas mixtures of C_2H_2/air=1/1 and of C_2H_2/O_2 =1/1 are shown in Figs. 5 and 6 respectively. In these figures the plots at 1kg/cm^2

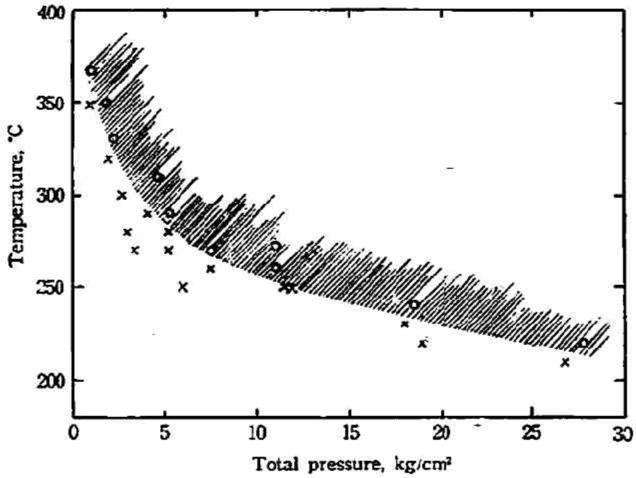

Fig. 5 The explosions of acetylene-air mixtures

(C_2H_2 : air=1 : 1)
O: exploded ×: not exploded

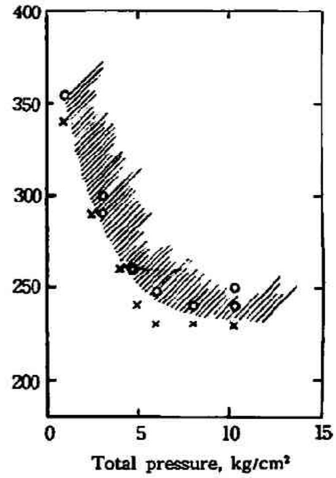

Fig. 6 The explosions of acetylene-oxygen mixtures
($C_2H_2 : O_2$=1 : 1)
O: exploded ×: not exploded

are cited from the results by Rimarski and Konschak's measurements and they coincide with the extrapolations of the curves of the present results and the results of the present experiment on the C_2H_2—air mixture coincide with those by Schläpher and Brunner[5] on the explosion of the mixture under up to 2.5 atm. The curvature of the curve of explosion temperature against the total pressure is larger in the case of $C_2H_2-O_2$ mixture than in that of C_2H_2—air mixture.

5) P. Schläpher and M. Brunner, *Helv. Chim. Acta*, **13**, 1125 (1930)

As described above, the violence of explosion of C_2H_2—air mixture was much weaker than that of C_2H_2—O_2 mixture, and even under the severest condition of the present experiment where the total pressure was 27.5 kg/cm^2, the maximum pressure of explosion was 58 kg/cm^2 and the sound of the explosion was scarcely heard. On the other hand, in the case of C_2H_2—O_2 mixture, the sound was clearly heard even in the explosion under the total pressure of 3 kg/cm^2. Though the effect of N_2 on the explosion limits is not yet so clearly elucidated as in the cases of CCl_4 and H_2O, but the addition of N_2 is considered to retard the propagation of the explosion.

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